

C. DIFFUSION THROUGH UNSATURATED TUFF

Direct and indirect techniques have been used during the last fifty years to measure or calculate diffusion coefficients in most porous media (Kemper 1986). Both techniques employ steady-state and transient-state methods of analysis. Fick's first law forms the basis for evaluating steady-state experiments, and Fick's second law, modified to account for the properties of porous media, is used for transient-state experiments. Diffusion coefficients in geologic media have traditionally been measured by tracer half-cell diffusion methods that monitor the transient diffusion front of a tracer species through the material of interest.

Unsaturated diffusion experiments involving blocks of tuff have also been proposed for the study of diffusion in Yucca Mountain tuff (Yucca Mountain Project study plan 8.3.1.3.6.2). A block of tuff is machined to prescribed dimensions, and a narrow hole is drilled to the center of the block. The porosity is determined by measuring the difference in weight between dry and saturated samples. After initial saturation, the block is allowed to dry until the desired moisture content is achieved. The block is then sealed in an airtight container and placed in a constant-temperature bath to allow the moisture distribution to equilibrate. It takes many months for the water to distribute evenly through the block because the permeability of Yucca Mountain tuff is low. The appropriate time for equilibration to occur could be calculated using a transport code. After equilibration, a solution containing radionuclides is placed in the bottom of the injection hole. The tracers are allowed to diffuse for a fixed period of time, then the block is frozen, sectioned, and each section analyzed. The distribution of radionuclides in the tuff matrix is fitted to a diffusion equation using a transport code, and diffusion coefficients as a function of saturation are determined.

Unsaturated conditions, or saturated conditions with very low water content, present unique exper-

imental problems. Diffusive fluxes through low-water-content materials require longer time periods to collect sufficient data from transient-state experiments. For diffusion coefficients less than 10^{-8} cm²/s, the time period can be months to years. For direct steady-state techniques, maintaining proper boundary conditions under unsaturated conditions over long time periods is extremely difficult and has not yet been satisfactorily demonstrated.

Therefore, an indirect method is needed that provides reliable diffusion coefficients. The most widely used indirect method is the measurement of electrical conductivity in a potentiostatic or galvanostatic mode, coupled with the Nernst-Einstein relationship, which provides reliable diffusion coefficients in electrolyte solutions (Miller 1972; Robinson and Stokes 1959). Fortunately, water-wet geologic materials are ideal for this method because the geologic media consists of an electrolyte solution dispersed throughout a nonconductive porous solid. Diffusion is completely dominated by the aqueous solution. Electrical conductivity is related to the migration of ions in the aqueous solution because the ease with which ionic species can migrate through an aqueous solution is exactly analogous to the ease with which the aqueous species can align their dipoles along the electric field vector, as long as the frequency is appropriate.

Soil scientists have developed multi-electrode methods for measuring electrical conductivity and salinity of porous media in the field and laboratory (Rhoades and Oster 1986; Gupta and Hanks 1972). The proven method of obtaining conductivity data is the use of a fixed excitation frequency conductivity bridge, based on its tested design, direct resistance and conductivity readouts, ease of operation, and availability.

A variation of the two-electrode method is ideal for the study of geologic media (Geddes et al. 1971). The electrical conductivity cells designed for this study have two stainless-steel cap electrodes in contact with the whole-rock cores. Although pla-

tinized electrodes are usually considered ideal for typical conductivity measurements, they are not recommended for solutions of low conductivity or with geologic materials (ASTM 1982). Stainless-steel electrodes have been shown to be appropriate for the low water contents and the current densities used in this experimental setup, that is, ≤ 1 mA/cm² (Geddes et al. 1971; Scott et al. 1967).

Electrical conductivity measurements of aqueous solutions actually measure the impedance (the AC analog of DC resistance) at the impressed frequency, which is a complex variable vector sum of the real in-phase (resistive) and the imaginary out-of-phase (reactive) components of the system response. For conductivity measurements (conductivity is the reciprocal of resistivity) using AC excitation, it is the in-phase component of impedance that is a measure of the true solution resistivity (or conductivity) and that can be used to represent the migration of ions in solution in geologic materials. Therefore, the impedance must be totally resistive, that is, no capacitive elements, for the Nernst-Einstein relationship to be applicable. This restriction has been verified for saturated and unsaturated geologic systems with a 1 kHz conductivity bridge using electrochemical impedance spectroscopy, which gives direct information about the real and imaginary components of impedance as a function of excitation frequency (Conca and Wright 1990). The impedance in geologic systems is a constant, frequency-independent quantity in the 600 to 7,000 Hz region, and is totally resistive in the 400 to 10,000 Hz region. Thus, the measured impedance at 1 kHz on geologic systems is a good measure of the true system resistance and its reciprocal, conductivity, and will give reliable values for diffusion coefficients calculated from the Nernst-Einstein equation. In addition, Wright (1990) determined $d(q)$ on the same soils using the electrical conductivity method and using Kemper's empirically derived relationship (Bresler et al. 1982), and the agreement was excellent ($R^2 = 0.99$). Once electrical conductivity measurements are made, they can be related to the diffusion coefficient through the Nernst-Einstein equation

(Jurinak et al. 1987; Conca and Wright 1990):

$$d_i = \frac{RT}{F^2} \cdot \frac{\Theta G t_i}{Z_i C_i}, \quad (71)$$

where d_i is the diffusion coefficient of the i th ion (cm²/s), R is the gas constant (J/deg mole), T is the absolute temperature (Kelvin), F is Faraday's constant (coul/mole), Θ is the cell constant for the conductivity cell sample holder (cm⁻¹), G is the measured conductance on the conductivity bridge (mhos), t_i is the transport, or transference, number of the i th ion ($t_{K^+} = 0.4898$ at 0.1 M; $t_{Na^+} = 0.3854$ at 0.1 M), Z_i is the charge number on the i th ion, and C_i is the molar concentration of the i th ion. The diffusion coefficients are corrected for solution nonideality using the extended Debye-Hückel approximation (Stumm and Morgan 1981). Effluent is monitored to correct for possible water/substrate interactions that can change the solution electrolyte concentrations.

The most effective way to determine diffusion coefficients under various degrees of saturation is to use the centripetal-acceleration UFA method (described in the "Solid-Rock Columns" section of Chapter V) to achieve hydraulic steady-state in the samples at target water contents using an appropriate electrolyte solution, for example, KCl or NaCl solutions in equilibrium with the tuff (Conca and Wright 1992b). Once steady-state has been achieved, the electrical conductivity is measured, and the Nernst-Einstein equation is used to determine the simple diffusion coefficient for that sample at that water content. The UFA method is then used to achieve another water content, and the diffusion coefficient is determined again. Simple diffusion coefficients in aqueous solution at 25°C for almost all chemical species, including organics, are between 0.5×10^{-5} cm²/s and 2.1×10^{-5} cm²/s (Conca and Wright 1992b; Oelkers 1991; Robinson and Stokes 1959). Therefore, simple diffusion coefficients in porous media that are less than 10^{-6} cm²/s at 25°C result from mechanisms or conditions other than the inherent mobility differences between the ions themselves. The variable d represents a generic simple diffusion coefficient at infi-

nite dilution that is a bulk property of the system and refers to the various combined physical effects of the porous media. The variable, thus, differs from the apparent diffusion coefficient, d_a , which includes retardation and other transient chemical effects and is specific for each species, medium, and fluid composition. Numerical models using $d(q)$ as an input parameter require the simple diffusion coefficient. Once breakthrough has occurred for a particular species, retardation ceases and the diffusion coefficient attains the simple value, which can be orders of magnitude higher than the apparent diffusion coefficients for many species in materials such as zeolitized tuff. The point at which breakthrough occurs is determined by the capacity of the flow paths in the media for that species under appropriate conditions.

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